



**INDUSTRIAL APPLICATION AND USES OF CLAY
MINERALOGY IN OIL AND GAS INDUSTRY.**

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30th October, 2017.

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PTG 311 CLAY MINERALOGY AND DIAGENESIS

Industrial Application of Clay mineralogy in Oil and Gas Industry

APPLICATION OF CLAY MINERALOGY IN OIL INDUSTRY:

Introduction:

Before we jump into Application of Clay mineralogy, it is important to answer some important Questions such as: What is a clay?, Why we Study Clay Mineralogy? And are clay minerals important or not?

What is a clay? - Clay can mean many different things depending upon who is using the term. But the definition of clay was first formalized in 1546 by Agricola. It has been revised many times since, although the fundamentals involving plasticity, particle size and hardening on firing were retained by most. AIPE Conference held in Brussels in 1958 and Copenhagen in 1960 adopted the following definition of clay minerals of crystalline structure: Clay minerals of crystalline structure are the hydrated layered silicates (packets), formed from a layer containing a silicon-oxygentetrahedral arranged in hexagons, which are connected with the layers of octahedral formed; clay minerals are usually fine-grained, and are capable of forming with water a more or less plastic mass.

However, in geology and soil classification, the term clay includes all particles that are $<2\ \mu\text{m}$ irrespective of their mineralogy (they could even be organic). This is strictly an operational definition, defined by the process of sedimentation as a means to separate particles. The clay fraction is thus the fraction that is smallest, most colloidal, and generally has the largest specific surface area. (Civil engineering also defines clay as a particle size, but using a different particle size than soil classifiers).

In mineralogy and soil chemistry, clay refers to a specific suite of minerals with layered structures. In greek, "phylon" means leaf and "phyllo-" came to mean layered. When it was found that clay minerals are layered structures they were called **phyllosilicates**.

Are clay minerals important? _ Clay minerals are an extremely important group of minerals. Due to the specific properties such as plasticity, hydration and catalytic properties, clay minerals are used in many industries. Agriculture, chemistry, pharmacy, refractory technology, ceramics etc. are the fields in which clay minerals found practical application. Estimates place clay minerals as comprising some 15% of the volume of the earth's crust. In soils, clays are generally the most important adsorbents for inorganic metals and often for organic solutes as well. This is because of their very high surface areas. Thus the presence and activities of clay minerals are critical to the plants on which we depend for primary production of our food.

Therefore, we can conclude that clay mineralogy is important to us, and the Question of why we study it is because of its crucial importance.

Industrial Application of Clay mineralogy and its Uses in general:

Clays are perhaps the oldest materials from which humans have manufactured various artifacts. The making of fired bricks possibly started some 5,000 years ago and was most likely humankind's second earliest industry after agriculture. Such microporous materials as zeolites and clay minerals have many applications in the industrial sector. They can be used as catalyst carriers, catalysts themselves, molecular sieves, and sorbents. They have a tremendous number of miscellaneous uses, and for each application a distinct type with particular properties is important. Clays composed of kaolinite are required for the manufacture of porcelain, whiteware, and refractories. Talc,

pyrophyllite, feldspar, and quartz are often used in whiteware bodies, along with kaolinite clay, to develop desirable shrinkage and burning properties. Sodium smectites are therefore used as rheology control agents because of the colloidal structure their delaminated particles form in water. Recently, clays have become important for various aspects of environmental science and remediation. Dense smectite clays can be compacted as bentonite blocks to serve as effective barriers to isolate radioactive wastes. Smectites can also absorb polar liquids other than water and will accommodate organic cations in exchange for their native counterions. This enables them to be used as absorbents and as rheological agents in nonaqueous systems. Tons of kaolinite clays are used as paper fillers and paper coating pigments. Palygorskite-sepiolite minerals and acid-treated smectites are used in the preparation of no-carbon-required paper because of the colour they develop during reactions with certain colourless organic compounds. The intercalation of smectites with hydroxy-metal polycations is a method of mineral modification developed in the late 1970s. The United States is the world's largest producer of both bentonite and kaolinite. Turkey, Greece, and Brazil are also large producers of bentonite. and Uzbekistan, Greece, and the Czech Republic are major suppliers of kaolinite.

With so many clays in the earth's crust, it is natural that we have found many other uses for them than their rather passive role in agriculture and forestry. Let us discuss briefly about the role of Clay in mining Industry before our main target (i.e. Oil and Gas Industry).

1. IN MINING INDUSTRY

According to the U.S. Geological Survey (<http://minerals.usgs.gov/minerals/pubs/commodity/clays/>), in 1998 there were about 770 active open-pit clay mines in 44 states of the U.S. These mines were operated by some 240 companies which employed some 13,700 people in clay mining and milling, and these companies sold 43.0 million metric tons of clay products for \$2.14 billion. Michigan is a very modest clay producing state, producing about 725,000 metric tons of "common" clay for a market value of \$3.82 million.

In clay industry, it is typical to divide mined clays into the following groups:

1. Ball clay: The principle markets and uses for "ball clay" are for **making wall and floor tiles, "sanitary ware"** which is ceramic plumbing fixtures like sinks and toilet bowls, pottery, and adsorbents. Prices average about \$45 per ton, with a maximum near \$210 for the highest-quality ball clays.

2. Bentonite: Bentonite is used as **drilling mud for oil and gas exploration**, to make foundry casts in metallurgical industries, as kitty litter, as a pelletizing agent for iron ores, as filters and adsorbents, for waterproofing and sealing, as a thickening agent, and even as animal feeds. Prices average about \$40 per ton, with the best grades bringing prices near \$480.

3. Common clay: These are the clays used to make heavy items that do not require a particularly pure deposit, and these are the types that are mined in Michigan near Lake Erie. Common clays are used for **construction bricks, portland cement** and lightweight aggregate for concrete, for drain tile, flue linings, and sewer pipe, and for terra cotta. Prices average about \$6 per ton, with a maximum near \$15.

4. Fire clay: Fire clays are those that are used primarily in **refractory (heat tolerant or fire-resistant)** applications, such as **bricks, blocks**, and **mortar** for fireplaces, incinerators, and **power plants**. Some fire clays are also used for pottery. Prices average about \$18 per ton, with high-quality clays near \$115.

5. Fuller's earth: This is the name given to a variety of attapulgite and montmorillonite clays that are similar to the bentonites and used for similar purposes. Thus, Fuller's earth is used as **kitty litter ("pet waste adsorbents") oil and grease adsorbents and filters, pesticide and fertilizer carriers, and as flow control agents for animal feeds**. More minor uses are as drilling muds, cements and adhesives, and pharmaceutical carriers. Prices average about \$113 per ton, with prices for the best grades near \$170.

6. Kaolin: Kaolinite is a white clay that has long **been used to coat paper and make it smoother, bulkier, and whiter**. Kaolin clays are also used for fire-resistant bricks, in fiberglass, in paints, in rubber tires, and to make catalysts. Prices average about \$110 per ton, with the best pigment grades bringing \$325 after processing.

2. In Oil and Gas Industry

In recent years, clay minerals have gained in importance in the oil & gas industry, where are used as a basic component in drilling fluid technology. Clay minerals e.g. chlorite, smectite, illite, kaolinite, etc. are present in the targeting rocks of oil and gas exploration. During the early age (1940s and 1950s) of worldwide oil exploration, clay minerals were studied to predict the quality of organic rich source rock and generation mechanism when scientists tried to investigate the origin of oil and gas (Grim, 1947, Brooks, 1952). Then the **clay minerals analysis was used as a tool in terms of environmental determination, stratigraphic correlation and hydrocarbon generation zone identification to find exploration target interval**, which was preliminarily and generally summarized by Weaver in 1960. By the 1970s, the clay minerals began to be widely studied **for diagenesis and reservoir quality prediction due to the application of petrological analysis and quantitative mineralogical analysis by X-ray diffraction** (Griffin, 1971; Pettijohn, 1975; Heald and Larese, 1974; Bloch et al., 2002). Since 1980s, the clay minerals analysis has been **used to determine the hydrocarbon emplacement time and petroleum system analysis** (Lee et al., 1985). These intermittent clay minerals research progresses are the result of exploration demands of conventional reservoirs (sandstone and carbonate rocks) at different times.

Clay minerals plays an important role in oil and gas exploration from many points of view: basin tectonic evolution, depositional environment, thermal history and maturation history of organic matter in the source rock, hydrocarbon generation, migration and accumulation process, diagenetic history and reservoir quality prediction. The traditional and cutting-edge analytical tools and techniques are also be introduced to identify and characterize the clay mineralogy, rock fabrics property and micro- to nano-scale pores both conventional and unconventional oil and gas exploration.

The clay minerals are **important compositions in source rocks and reservoir rocks** that can generate and store oil and gas respectively. The presence of clay minerals strongly influences the physical and chemical properties of conventional sandstone, carbonate and unconventional shale.

The modern innovative technologies have been playing key roles in the identification and quantitative characterization of clay minerals, **which help define the best brittle reservoir interval and avoid exploration failure by choosing the compatible drilling and hydraulic fluids**.

The number of applications for the clay minerals kaolinite, Na- and Ca-montmorillonite and sepiolite continues to expand. New and improved processing, continued research and development and new market opportunities will require continued exploration and development of new deposits in all areas of the world.

2.1 Indication of tectonics and sedimentation

During the evolution of petroliferous sedimentary basin, **the clay minerals contained in the rocks undergo a series of changes in composition and crystal structure in response to tectonics and sedimentation**. For example: the depth distribution of illite/smectite (I/S) compositions showed an irregular, zig-zag trend with depth. This trend is probably the result of multi-stage reverse faultings resulted from the compressional tectonic movement. Therefore, Clay mineral can be used to **infer tectonic/structural regime, basin evolution history and the timing of various geologic events**. This may even provide useful tool in helping to unravel the histories in tectonically complex area.

2.2 Indicator of hydrocarbon generation and expulsion

One of the most important task in oil and gas exploration, is at least to confirm whether the exploration area has potential source that can generates the oil and gas or not. This drives geologists to study the potential source rocks (usually organic rich shales) to understand **if the organic matter in the source rock can generate hydrocarbons at a given depth in a specific geologic time, and when the generated hydrocarbons can reach the expulsion peak**. Organic geochemistry is the main discipline for studying oil and gas generation and expulsion. **However, clay mineralogy is also important for evaluation of these parameters for two reasons:**

1. clay minerals and organic matters usually coexist in the sedimentary rocks and
2. the ultrafine clay minerals are sensitive to the changes in the rocks accompanying the hydrocarbon generation and expulsion processes.

Clay minerals in shales concentrated organic constituents by adsorption to form abundant source material, and subsequently acted as catalysts in petroleum generation (Clay speed up the generation of Petroleum). Therefore, association of clay minerals and organic matter in shales is a significant factor in petroleum genesis.

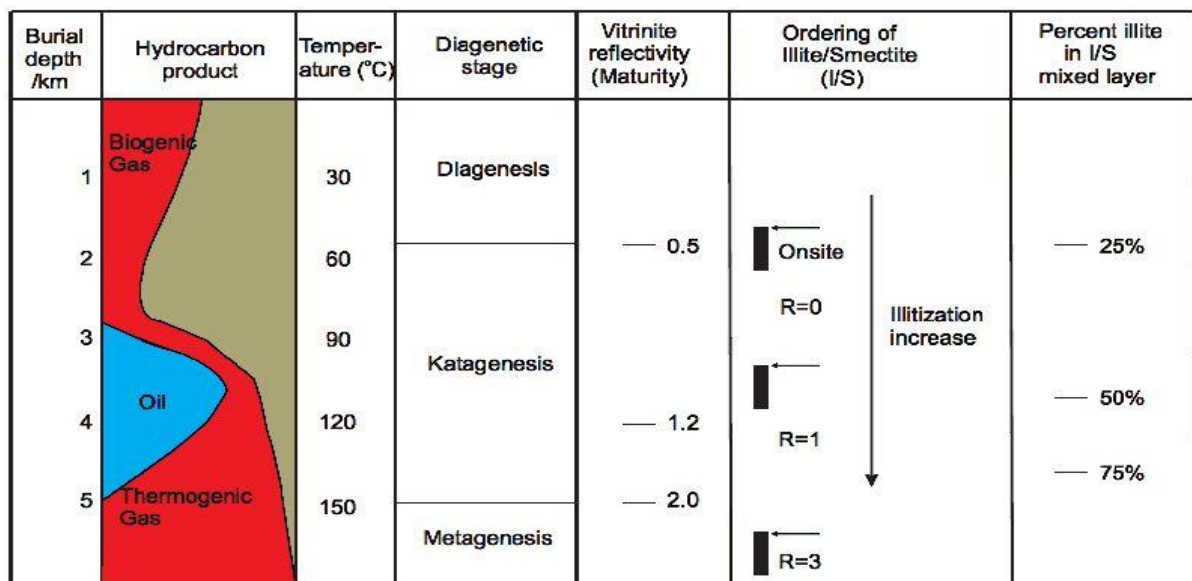


Figure 1. Generalized relationship between temperature, hydrocarbon generation, diagenesis, source rock maturity (vitrinite reflectance), and changes in mixed-layer illite/smectite. Figure and data summarized from Foscolos et al (1976), Hoffman and Hower (1979), Waples (1980), Tissot and Welte (1984).

The table above indicates the significant changes of clay minerals during burial and their relations with *diagenetic stages, temperature, organic matter maturity, hydrocarbon generation and expulsion*.

The Maturity of the Source Rock and the generation of oil and gas:

The maturity of the source rock and the generation of the oil and gas can be determined or indicated by:

1. vitrinite reflectance (R_o)

2. And the percentate of illitic beds in illite-smectite mixed-layer clay minerals

➡ **During early diagenesis**, the maturity of source rock is low, this is indicated by *low vitrinite reflectance (R_o)*, $R_o = 0.5\%$ and *low percentate of illitic beds in illite-smectite mixed-layer clay minerals, around 25% illite presence*. The Clay minerals mainly experience loss of pore water during this period. Therefore, during early diagenesis, $R_o = 0.5\%$ approximately corresponds to around 25% illite presence **INDICATING LOW MATURITY and LITTLE OIL IS GENERATED DURING THIS PERIOD.**

➡ $R_o = 0.5$ to 1.0% corresponding to 25 to 50% illitic beds in illite-smectite mixed-layer clay minerals **INDICATES MAJOR OIL GENERATING ZONE.**

➡ $R_o > 1.5\%$ corresponding to more than 75% illitic layers present in illite-smectite mixed-layer clay minerals **INDICATES CRACKING OF HYDROCARBONS FORM DRY GAS.**

This general trend can be used to predict if the source rock is able to generate hydrocarbon in an area. For example, *the smectite alters to illite at temperature of 80 to 120°C, which corresponds to the oil generation peak at the same temperature range.*

In conclusion we said, the change in maturity of organic matter and reaction progress in the smectite to illite transformation, which indicates that rapid increase in illite and decrease in smectite (montmorillonite) in I/S correspond to rapid oil generation.

2.3. Indices for hydrocarbon migration and accumulation

It is critical to establish that hydrocarbon formation and migration occurred after the formation of the trap (anticline, etc.). **Clay mineral-kerogen complex** plays a role in modifying hydrocarbon compositions during migration. During burial diagenesis, there is a gradual transformation of smectite to illite, dehydration which accompanies the transformation process indicates two things:

This firstly suggests that the replacement of kaolinite by illite or direct precipitation of illite indicates fluid flow where the chemical potential of the fluids is in disequilibrium within the reservoir sandstone. The existence of secondary illite does indicate aqueous fluid flow and thus can be used as indices of fluid movement and hence signal the possible hydrocarbon migration.

Secondly, it indicates that the water release could create a flushing action responsible for the migration of petroleum hydrocarbons from the source rock through the migration paths to nearby reservoirs. Also, the water liberation can build up abnormal pressures in less permeable sediments, which can provide migration dynamic for hydrocarbons.

Moreover abnormal Illite distribution has been used as an index to determine if certain rocks/strata/areas are a **hydrocarbon migration pathway and its conducting capability**. Abnormal illite distribution indicates that the hydrocarbon migration happened.

The figure 3 below shows illite abnormal distribution of three wells from three different structure zones in **Liaodong Bay Sub-basin of Bohai Bai Basin in Northeast China**.

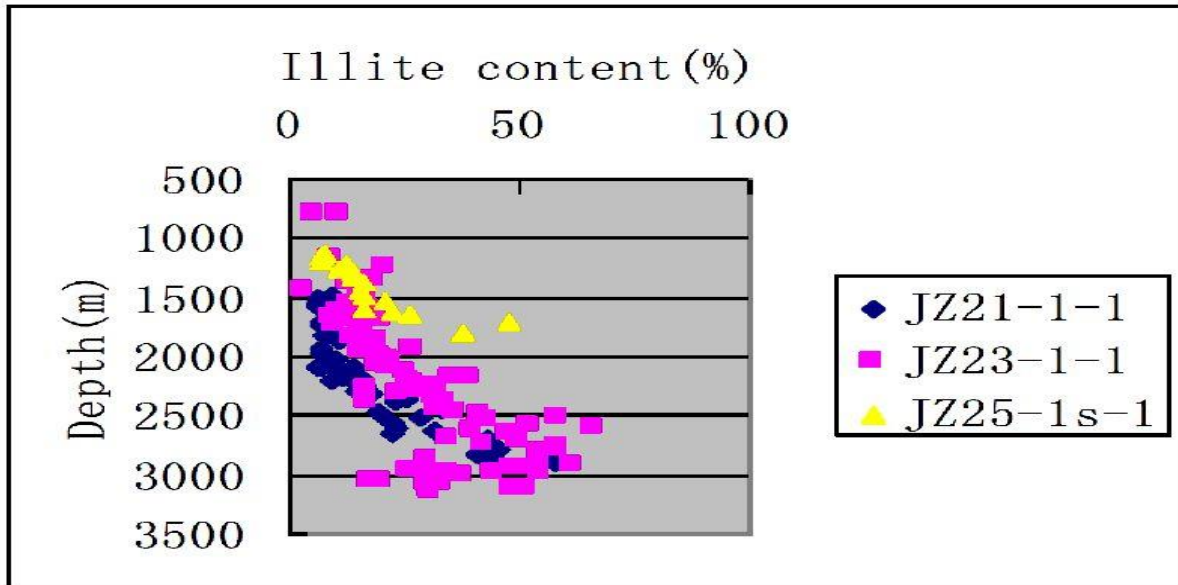


Figure 3. The illite content distribution versus depth from three wells in Liaodong Bay area, Bohai Bay Basin.

The figure 3 above suggests hydrocarbon migration happened in these three areas represented by three wells: **JZ21-1-1**, **JZ23-1-1**, and **JZ25-1s-1**, but **the conducting capabilities are different in the three areas based on different abnormal magnitude of illite content**. At the same depth (let say 1700 m) of these three wells, **illite content of well JZ25-1s-1 is the highest and the illite content of well JZ21-1-1 is the lowest, which indicates the hydrocarbon migration in the JZ25-1s-1 well area is the most active and the JZ21-1-1 area is the relatively least active area regarding to hydrocarbon migration** (Figure 3).

Therefore, we can conclude:

JZ25-1s-1 well is the largest hydrocarbon migration and accumulation area, and it contributes to the most reserves.

JZ23-1-1 well is second largest hydrocarbon migration and accumulation area.

JZ21-1-1 well has poor hydrocarbon migration pathway and poor conducting capability.

HYDROCARBON MIGRATION PREVENTION

The smearing of clay minerals can also prohibit the hydrocarbons' further migration and facilitate the hydrocarbon accumulation. When the soft clays are smeared into the fault plane during movement, they will provide an effective seal which prevent the further hydrocarbon migration and increase its accumulation. In many cases, the presence of clay types and their proportions can even indicate if there is oil and gas accumulation.

2.4. Significance of clay mineralogy for reservoir Quality prediction.

The quality of a reservoir is defined by its **hydrocarbon storage capacity** and **deliverability**. The hydrocarbon storage capacity is characterized by the **effective porosity** and the size of the reservoir, whereas the deliverability is a function of the **permeability**.

Porosity and permeability are the most important attributes of reservoir quality. They determine the amount of oil and gas a rock can contain and the rate at which that oil and gas can be produced. Most sandstones and carbonates contain appreciable fine-grained clay material including kaolinite, chlorite, smectite, mixed layer illite-smectite and illite. These clay minerals commonly occur as both detrital matrix and authigenic cement in reservoir sandstones. **The reservoirs initially have intergranular pores that are main space for oil and gas accumulation.** When the reservoirs are deposited, their primary porosity is frequently destroyed or substantially reduced during burial compaction. The clay minerals are usually assumed to be detrimental to sandstone reservoir quality because **they can plug pore throats as they locate on grain surface in the form of films, plates and bridge and some clay minerals promote chemical compaction.** **Not only in sandstone reservoir, but also in limestone reservoir, the clay content greatly accelerated the rate of porosity loss.** Generally, the porosity loss is mainly caused by the diagenetic process including mechanical compaction, quartz and K-feldspar overgrowths, carbonate cementing and **clay mineralization**. Especially, **the diagenetic clay minerals** play a very important role in determining the reservoir quality.

Authigenic clays from diagenesis in the sandstones studied occur as *illite, illite-smectite and kaolinite*. They form cements around the detrital minerals. **During the period of intermediate to deep burial diagenesis, illite and illite-smectite clays are the first cements.** These early-formed clay films play an important role in reducing reservoir porosity and permeability during burial diagenesis. Moreover, illitic clays usually occur as pore-bridging clays to reduce the pore space and block the fluid movement by **reducing permeability**.

The positive aspect of clay in oil reservoir.

The existence of clay minerals does not always mean to reduce the reservoir quality, it may be good phenomenon to indicate good reservoir quality, e.g., coats of chlorite on sand grains can preserve reservoir quality because they prevent quartz cementation (Heald and Larese, 1974; Bloch et al., 2002; Taylor et al., 2004). Sometimes, the higher content zone of kaolinite is indicative of higher porosity. The reason is that porosity is created when the acid dissolves feldspar to produce kaolinite (Jiang et al., 2010).

2.5. Petroleum emplacement chronology

Petroleum emplacement chronology is one of the frontier research subjects in both petroleum geology and isotope geochronology. Determining the oil or gas emplacement ages has important implications for oil or gas genesis and resource prediction. Typical relative chronology for oil or gas migration, emplacement, and accumulation is established by petrology, basin tectonic evolution, trap formation, and hydrocarbon generation from the source rock (Kelly et al., 2000; Middleton et al., 2000). So far, the illite K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique hold significant promise in establishing absolute constraints on the emplacement age of oil and gas.

Since the middle of the 1980s, authigenic illite K-Ar dating has been applied to determine the ages of petroleum migration in the North Sea oil fields and Permian gas reservoirs in Northern Germany (Lee et al., 1985; Liewig et al., 1987, 2000; Hamilton et al., 1989). **The dating is based on the hypothesis that "illite is commonly the last or one of the latest mineral cements to form prior to hydrocarbon accumulation.** Because the displacement of formation water by hydrocarbons will cause silicate diagenesis to cease, K-Ar ages for illite will constrain the timing of this event and also constrain the maximum age of formation of the trap structure" (Hamilton et al., 1989).

2.6. Significance for petrophysical property study

The reservoir petrophysics e.g. porosity, permeability, water saturation and hydrocarbon saturation are the most important properties that define and control qualitatively and quantitatively the reservoir performance. The minerals present in the reservoir especially **the clay mineral** can play the utmost role, which affects both the reservoir capacity and production because the grain size of clay minerals is generally very small and result in very low effective porosity and permeability, thus any presence of clay in a reservoir may have direct consequences on the reservoir properties.

There are many characteristics of clays that strongly affect their electrical behaviour, Characteristics like composition, internal structure, the tremendous surface to volume ratios of most clays and the charge imbalance along the surface of clay minerals are manifestations that have an impact upon the interpretative petrophysical parameters by well logging responses. In order to better understand the well logging response for petrophysical analysis, **the type of clay minerals must be taken into account in reservoir evaluation.** For example:

Potassium presence in the reservoir can increase radiation on Gamma Ray logs. Sometimes, the log response can indicate the hydrocarbon saturation and clay content, e.g., **the high resistivity zone of resistivity log corresponds to intervals with low water saturation, a more restricted distribution of diagenetic clay (mainly chlorite) and the low resistivity zone corresponds to intervals with more widely distributed diagenetic clay and variably reduced permeability (Nadeau, 2000).**

Summary:

Clay minerals are thus used for two broad functions, and intensively studied in order to understand and improve their usefulness for those functions:

On the one hand, clays have environmental applications since they are present in most of the world's soils, sediments, waters, and even the air. Clays thereby capture the attention of agronomists and foresters who want to control nutrient uptake, soil tilth, fertility, and water relations. Civil and environmental engineers study clays because they influence the "plastic" properties of earth materials and are primary adsorbents that retard the mobilities of contaminants in the environment.

On the other hand, pure deposits can be dug up and shaped for many purposes in industry. Thus industrial chemists try to understand catalytic and adsorptive properties of the various clay minerals, their rheological properties as they apply to colloidal suspensions (paints, drilling muds), how to transport them and put them onto cellulose for paper, how to make better bricks and ceramics, and how they influence the behavior of nutrients and drugs when they are used for animal feed or pharmaceutical delivery.

Moreover, those concerned with resource exploration try to understand clays as indicators of weathering or depositional environment and as controllers of oil reservoir quality.

The clay minerals are important compositions in source rocks and reservoir rocks that can generate and store oil and gas respectively. The presence of clay minerals strongly influences the physical and chemical properties of conventional sandstone, carbonate and unconventional shale.

Regionally, the clay minerals can be used to interpret and understand such perspectives as the basin evolution on tectonics, sedimentation, burial and thermal history, to infer the sedimentary environment and to correlate strata, etc.

For clay minerals in source rocks, they are important for quality evaluation of the hydrocarbon generation, expulsion and migration. Clay minerals help concentrate organic matter by adsorption and subsequently act as catalyst to generate petroleum. The transformation of montmorillonite to illite and increasing ordering of I/S can indicate the hydrocarbon generation and expulsion events.

For clay minerals in reservoir rocks, their presence has an important impact upon reservoir properties such as porosity and permeability and upon those measured physical data that are used to evaluate reservoir quality. Geologists use clay minerals information to decipher the burial diagenetic process and reveal the pore type and pore evolution. Even though they are usually considered to be detrimental to reservoir quality because they can plug pore throats and can be easily compacted, other diagenetic processes may enhance porosity through the forming of secondary porosity through providing porosity by clay dissolution, creating micropores in clays and coating of chlorite on grains to prevent quartz cementation.

The recent emerging shale oil and gas exploration requires state-of-art imaging and characterization techniques to study the application of clay minerals in the exploration of this unconventional resource. The modern innovative QEMSCAN® and FIB/SEM/EDS have been playing key roles in the identification and quantitative characterization of clay minerals, which help define the best brittle reservoir interval and avoid exploration failure by choosing the compatible drilling and hydraulic fluids.

Of course, clay minerals are fascinating in their own right and need have no purpose!

Anyone who studies clays has access to a myriad of scientific resources. There is a Clay Minerals Society whose whole purpose is to share the study of clays.

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